

Crystallization characteristics of weakly branched poly(ethylene terephthalate)

Guang Li*, Sheng Lin Yang, Jian Ming Jiang, Cheng Xun Wu

State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, Donghua University, West Yan'an Road, Shanghai 200051, China

Received 23 February 2005; received in revised form 9 July 2005; accepted 27 August 2005

Available online 21 September 2005

Abstract

A series of branched poly(ethylene terephthalate) (BPET) samples were prepared from melt polycondensation by incorporation of various amount (0.4–1.2 mol%) of glycerol as a branching agent. These polymers were characterized by means of ^1H NMR, intrinsic viscosity. The general crystalline and melting behavior was investigated via DSC. It was found that the crystalline temperature T_{cc} from the melt shifted to high temperature and the T_{hc} from the glass got low for BPETs while the melting temperatures of BPETs kept almost unchanged. The kinetics of isothermal crystallization was studied by means of DSC and POM. It was found that the present branching accelerated the entire process of crystallization of BPETs, although prolonged the induced time. In addition, branching reduced nucleation sites; hence the number of nucleates for BPET got smaller. Therefore, more perfect geometric growth of crystallization and greater radius of spherulites could develop in BPET due to less truncation of spherulites.

© 2005 Published by Elsevier Ltd.

Keywords: Poly(ethylene terephthalate); Branched polymers; Isothermal crystallization

1. Introduction

With the progress in sophisticated synthesis methods, it becomes easier now to produce polymers with complicated macromolecular architecture [1–2]. As a matter of fact, the macromolecular architecture has become a tunable factor to change polymer properties and applications. Among different kinds of molecular architectures, branching shows unusual contributions to polymers for their rheological characteristic, crystalline behavior and processing properties, etc [3–5].

Poly(ethylene terephthalate) (PET) is an important polymeric material and is widely used in the form of fiber, film, plastic and so on. The commercial synthesized PET with a linear molecular structure (LPET) has low melt strength for applications such as direct blow moulding, vacuum forming and extrusion with drawing. However, when PET foams are formed, the high extensional viscosity should be designed to prevent foam collapse during the final stabilization phase of the extrusion process. Branched PET (BPET) could be expected to have greater melt strength by analogy with other branched

polymer such as low-density polyethylene. Yilmazer et al. studied viscoelastic characteristics of two chemically modified (chain extended and branched) PET resins and one unmodified PET resin. They found that the modified resins had lower melt flow index, higher die swell and storage modulus than the unmodified one, resulting in a better foaming characteristic in extrusion foam processing because of their elastic nature [6]. Moreover, BPET has also found its important application in high speed spinning fiber formation. Hess et al. found less oriented structure developed in BPET fibers than in LPET fibers under the same spinning speed, which would impeded stress induced crystallization and reduced the unstabilities of high-speed spinning [7].

Different methods have been explored to prepare BPETs. Multifunctional monomers such as trimethylolpropane, glycerol, trimesic acid and tetrafunctional pentaerythritol, etc. were once employed to produce BPET via polycondensation [8,9,10]. On the other hand, some potential functional monomers such as tetrafunctional epoxy-based modifier, ethylene/ethylacrylate terpolymer or glycidyl methacrylate, were also added into PET resin during melt extrusion processing to induce branching or a certain amount of crosslinking structure [11,12]. To avoid gelation when preparing BPET, Hudson et al. discussed the balance establishment of branching agent and end-capping agents such as benzyl alcohol, do-decanol [13].

* Corresponding author. Tel.: +86 21 627 53396; fax: +86 21 627 53396.
E-mail address: lig@dhu.edu.cn (G. Li).

Although the viscosity of BPET was greater than that of LPET [11,14], BPETs generally showed more remarkable shear thinning rheological behavior [10], longer relaxation time [14]. The study of dynamic rheology of BPET further explained the rheological characteristic of BPET and the difference between BPET and LPET [15]. Comparatively, the effect of branching on the crystallization behavior of PET has been scarcely investigated. The existent reports even showed almost opposite results about the crystallization characteristic of BPET [10,16,17]. Therefore, it is essential and important to reveal the relationship between the molecular architecture and the crystallization characteristics of the BPET for both applied and theoretical purpose.

In this study, the BPET samples were prepared from melt polycondensation by incorporating small amount of trifunctional glycerol (GL) as a branching agent. We focused our attention on the crystallization characteristic of these BPETs. The effect of branching on the crystalline and melting behavior, especially the kinetics of isothermal crystallization was investigated by DSC. The crystallization morphologies of both branched and linear samples were observed by means of POM.

2. Experimental

2.1. Preparation of branched poly(ethylene terephthalate)

BPETs were prepared via the ester interchange route starting from dimethyl terephthalate (DMT) and ethylene glycol (EG) with different amounts of trifunctional glycerol (GL) as a branching agent. Transesterification was performed at a maximum temperature of 220 °C, the subsequent polycondensation was carried out at a maximum temperature of 280 °C under vacuum. For all polymerization, the end time was chosen at the moment when a certain stirring power reached.

2.2. Measurements

The chemical composition of BPETs was analyzed by H^1 NMR (Avance 400 Bruker). D-trifluoroacetic acid was used as a solvent. The intrinsic viscosities of the obtained samples were measured in a phenol/tetrachloroethane mixture (1:1, weight ratio) at a temperature of 20 °C using an Ubbelohde viscometer. Differential scanning calorimetry (DSC, Perkin–Elmer Pyrist) was used to detect the heat flow from the samples during isothermal crystallization from the melt as well as usual crystalline and melting behavior. All the measurements were conducted under nitrogen atmosphere. For isothermal crystallization kinetics studies, all samples were first heated up to 280 °C and kept at this temperature for 3 min to remove any thermal history. Then, the samples were quenched to the predetermined crystallization temperature (213, 208, 203, 198 °C) at a cooling rate 100 °C/min. The change of exothermic enthalpy with time was recorded. For usual crystalline and melting behavior, samples were heated at the rate of 10 °C/min to 280 °C (the first heating) and kept 3 min at

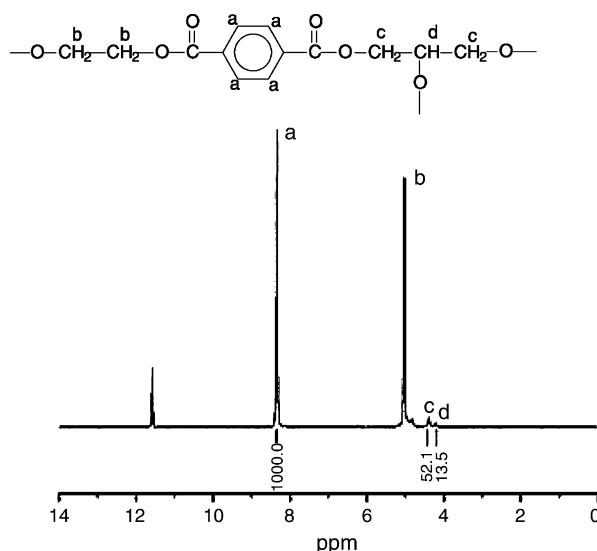


Fig. 1. The H^1 NMR spectrum of BPET-5.0.

this temperature, then cooled at the same rate to the room temperature, finally heated again beyond the melting (the second heating). An Olympus BX51 polarized optical microscope (POM) with a heater was used to observe the crystallization morphologies of samples. All samples were first heated to 280 °C and kept 5 min, then quenched to 220 °C. The development of crystallization morphologies at the set temperature 220 °C with time was observed and recorded automatically.

3. Results and discussions

3.1. Chemical composition of branched PET

The H^1 NMR spectrum of the BPET with 5 mol% GL addition was illustrated in Fig. 1. There are four peaks in the spectrum which correspond to four kinds of protons: i.e. proton a, b, c and d as labeled in the macromolecular structure of BPET in Fig. 1. Furthermore, the ratio of proton c area over proton a area is about 5 mol%, matching the feed mole ratio of GL over DMT, so it could be concluded that GL was stoichiometrically linked into macromolecular chains of PET.

The numbering of samples, their feed composition as well as the intrinsic viscosities were listed in Table 1. The more content of GL, the higher the intrinsic viscosities was, which meant the higher molecular weight or more branching with increasing of GL loading.

Table 1
The intrinsic viscosities, feed composition ratio of all samples

Samples	Composition ratio DMT:GL (mol ratio)	Intrinsic viscosity $[\eta]$ (dL g ⁻¹)
LPET	1:0	0.656
BPET-0.4	1:0.004	0.695
BPET-0.8	1:0.008	0.734
BPET-1.2	1:0.012	0.746

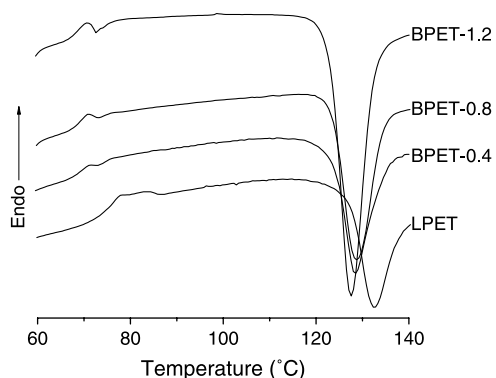


Fig. 2. DSC curves of all samples during the first heating.

3.2. DSC analysis of branched and linear PETs

Crystalline polymers could develop crystallization both from the melt and from the glass state. When the temperature is beyond the glass transition temperature, they could crystallize from the glass. The crystallization from the glass is governed by diffusion of polymer chains compared with that from the melt. From the first heating scanning curves (Fig. 2), it was obvious that the heating crystalline temperatures (T_{hc}) of BPETs from the glass reduced compared with that of LPET. Furthermore, the cooling crystalline temperature (T_{cc}) of BPETs from the melt shifted to higher temperatures (Fig. 3). Therefore, it could be known that BPETs crystallize more easily than LPET both from the melt and from the glass. These results were accordant with those of Oh et al. [10], but not agreeable with what Jayakannan and co-workers found [16]. Jayakannan et al. studied crystallization behavior of branched PETs with high concentration (1.4–5.0 mol%) of tri-functional aromatic monomer as a branching agent using DSC at different cooling processing. They found that crystalline temperature (T_{cc}) of branched PET was lower than that of linear PET at every cooling rate (2–10 °C/min), and more introduction of branching agent made T_{cc} much lower.

The melting temperatures T_m of BPETs showed almost unchanged, as illustrated in Fig. 4. The melting enthalpy (ΔH_m) increased when GL was introduced in a small amount (0.4–0.8 mol%) but decreased as more GL (1.2 mol%) was added, which was in accordance with the Jayakannan and co-workers' work [16]. The dependence of T_{cc} , T_{hc} , T_m , and ΔH_m

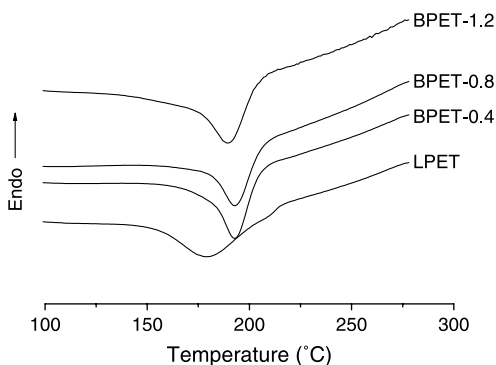


Fig. 3. Crystallization peaks of DSC during cooling from the melt.

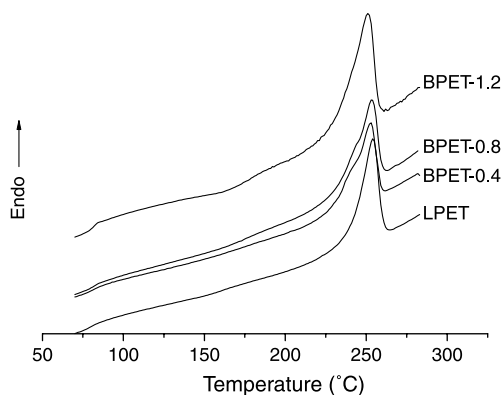


Fig. 4. Melting peaks of DSC for all samples from the second heating.

on the GL content was an indication of complicated influence on PET crystallization behavior brought by incorporating GL to PET macromolecular chains. From Fig. 2 it could also be seen that the glass transition temperatures of BPETs decreased, which meant that the motion of chain segments of BPETs got easier compared with LPET.

The characteristic data of samples from DSC were listed in Table 2. It looks like that 0.4–0.8 mol% GL introduction was mostly in favor of crystallization development.

3.3. Kinetics of isothermal crystallization from the melt

The expression mostly used for the analysis of the kinetics of isothermal crystallization is the Avrami equation,

$$1 - x(t) = \exp(-k(T)t^n) \quad (1)$$

where $x(t)$ is the crystallization transformation developed after time t , $k(T)$ is the crystallization rate constant associated with the rate of nucleation and growth and n is the Avrami exponent, the values of which depends on the primary nucleation and growth geometry of the crystalline entities. The values of n and $k(T)$ are usually obtained from the double logarithmic form of above equation,

$$\ln[-\ln(1 - x(t))] = \ln k(T) + n \ln(t) \quad (2)$$

When DSC is used to study isothermal kinetics, $x(t)$ could be related to the ratio of exothermic enthalpy ($\Delta H_c(t)$) at time t over totally exothermic enthalpy ($\Delta H_c(\infty)$) after infinite time period. While crystallization develops at a predetermined

Table 2
The characteristic data of samples from DSC

Samples	$T_{hc}/^{\circ}\text{C}$	$T_{cc}/^{\circ}\text{C}$	$T_m/^{\circ}\text{C}$	$\Delta H_m/\text{mJ mg}^{-1}$	$T_g/^{\circ}\text{C}$
LPET	132.5	179.8	254	42.1	77.8
BPET-0.4	128.5	193.3	253	43.6	71.5
BPET-0.8	128.7	193.8	253	44.5	71.2
BPET-1.2	127.6	190.8	251	35.6	70.6

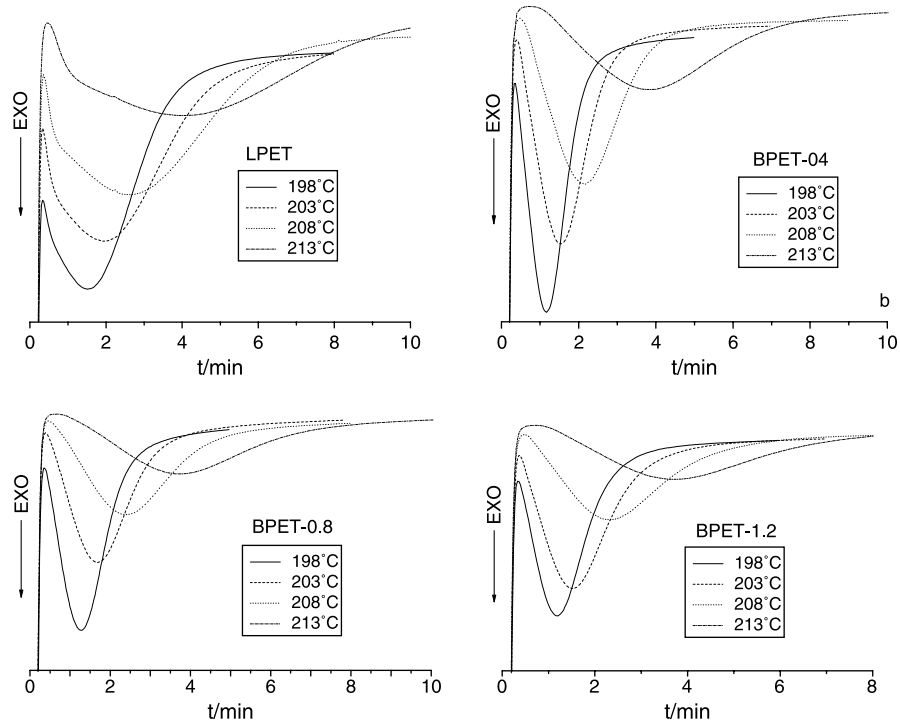


Fig. 5. The experimental crystallization exothermic curves of LPET and BPETs at different predetermined crystallization temperatures.

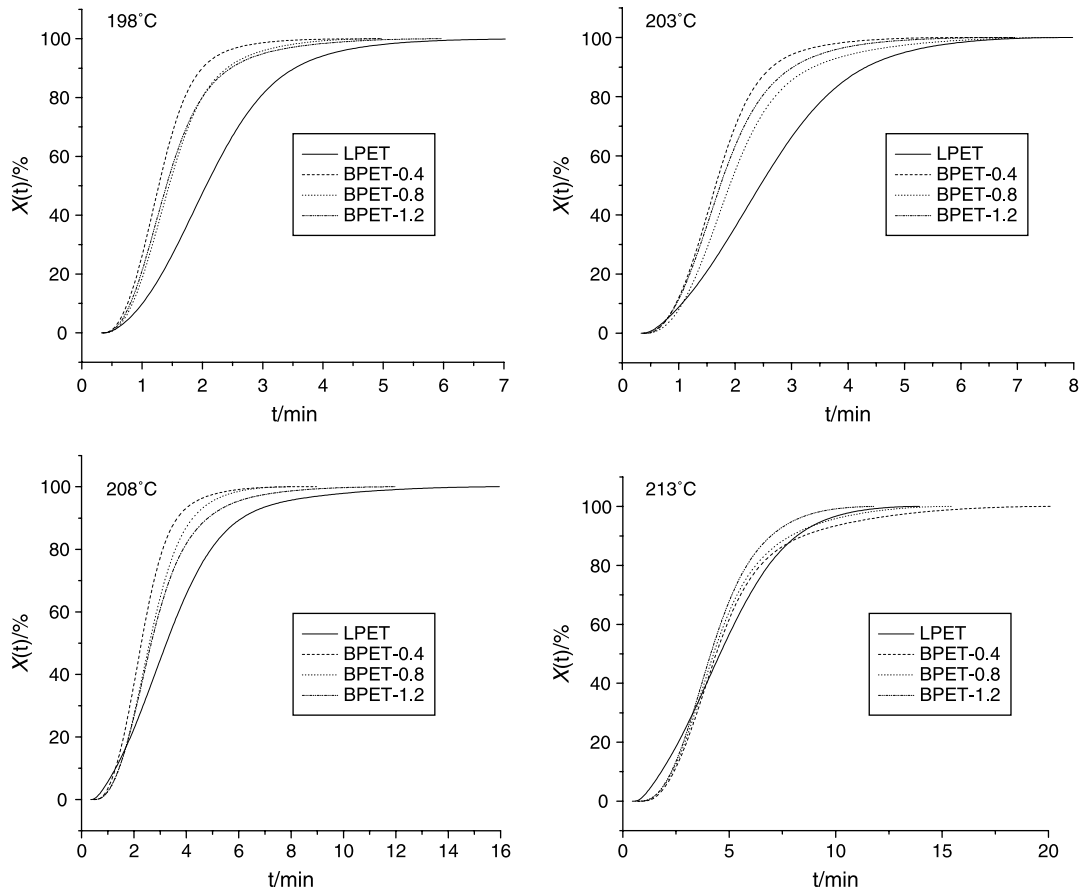


Fig. 6. The dependence of crystallization transformation on time.

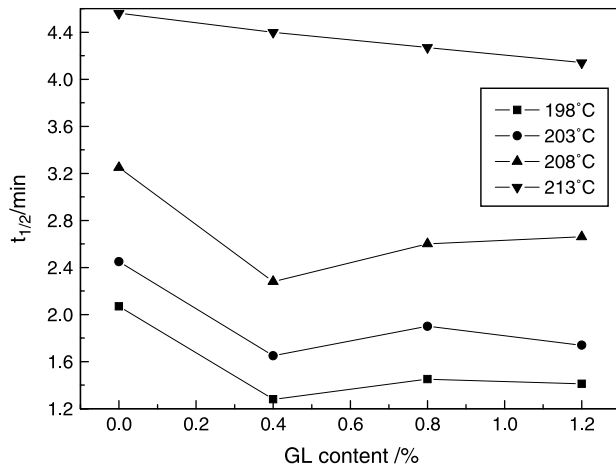


Fig. 7. The change of half time with GL content.

temperature T , there is

$$x(t) = \frac{\Delta H_c(t)}{\Delta H_c(\infty)} = \frac{\int_0^t dH_c(t)dt/dt}{\int_0^\infty dH_c(t)dt/dt} \quad (3)$$

According to the definition of the half time of crystallization, when $x(t)=50\%$, $t_{1/2}=(\ln 2/k(t))^{1/n}$, on the other hand, the fastest crystallization time, t_{\max} , can also be obtained from Eq. (1) after twice differentiation, which reads $t_{\max}=[(n-1)/nk]^{1/n}$.

The experimental crystallization exothermic curves of all samples were given in Fig. 5. The exothermic peaks became sharper with the addition of GL, especially when GL was present in very small concentration (0.4–0.8 mol%). This illuminated that BPETs could finish crystallization in a short time. The dependence of $x(t)$ on time at certain temperature for different samples was plotted in Fig. 6. It was revealed clearly that the

crystallization rate of BPET was generally enhanced with incorporation of small amount of GL, especially at low crystallization temperature. At high crystallization temperature, BPETs displayed longer induced time before crystallizing and low crystallization rate at early stage of crystallization. When crystallization transformation reached up about 30%, BPET crystallized faster than LPET. But this enhanced rate of crystallization was not proportional to GL concentration, as the change of $t_{1/2}$ with respect of GL content shown in Fig. 7. It was agreeable with the results in Table 2, i.e. the introduction of 0.4% GL increased the rate of crystallization markedly. This may be attributed to the complex influencing of branching on the crystallization behavior (discussed later). Fig. 7 also showed that for all samples, half time of crystallization increased with the increasing crystallization temperature, which was identical to the experimental results of Fig. 5. That is, during the chosen crystallization temperature region (198–213 °C), the rate of crystallization increased with the decrease of temperature. Furthermore, when crystallization temperature was high enough, for example 213 °C, the discrepancy of crystallization rates between BPET and LPET got smaller.

From these $x(t)$ values, $\ln[-\ln(1-x(t))]$ could be plotted versus $\ln(t)$. The values of Avrami exponent n , the crystallization rates $k(T)$, were obtained from the slopes and intercepts of these lines. These values as well as $t_{1/2}$, t_{\max} were listed in Table 3.

One of major differences found from Table 3 was the n values of BPET and LPET. The values of n for LPET were found to be between 2 and 3, whereas 3–4 for BPETs. The n values were associated with the nucleation mechanism, the dimensions of growth during crystallization. No any additives were loaded as nucleating agents, and the chemical composition between BPET and LPET was the same, so the nucleation mechanism for both BPET and LPET should be

Table 3

The values of Avrami exponents n , rate constant k , half time $t_{1/2}$ and maximum time t_{\max} of crystallization at different crystallization temperatures

Samples	k (min^{-1})	n	$t_{1/2}$ (min)		t_{\max} (min)	
			Experiment	Calculated	Experiment	Calculated
LPET						
198 °C	0.12	2.5	2.07	2.1	1.5	1.9
203 °C	0.09	2.3	2.45	2.5	1.92	2.2
208 °C	0.07	2.1	3.25	3.3	2.65	2.7
213 °C	0.03	2.1	4.56	4.6	4.08	3.9
BPET-0.4						
198 °C	0.27	3.7	1.28	1.3	1.17	1.3
203 °C	0.12	3.5	1.65	1.7	1.53	1.7
208 °C	0.04	3.4	2.28	2.3	2.16	2.3
213 °C	0.01	3.0	4.40	4.5	3.9	4.5
BPET-0.8						
198 °C	0.18	3.7	1.45	1.4	1.28	1.4
203 °C	0.08	3.4	1.90	1.9	1.65	1.9
208 °C	0.03	3.4	2.60	2.6	2.37	2.6
213 °C	0.01	3.3	4.27	4.2	3.70	4.2
BPET-1.2						
198 °C	0.23	2.7	1.41	1.5	1.20	1.4
203 °C	0.14	2.7	1.79	1.8	1.53	1.7
208 °C	0.05	2.5	2.66	2.8	2.31	2.7
213 °C	0.01	2.8	4.14	4.3	3.72	4.2

Table 4
The induced time observed from POM at 220 °C

Samples	The induced time/s
LPET	8
BPET-0.4	16
BPET-0.8	26
BPET-1.2	33

the same as homogeneous nucleating. It could be deduced that different n may be attributed to various dimensions of crystallization growth between PBET and LPET. Considering the macromolecular chain conformation, the dependence of half time of crystallization with respect to GL content, the induced time difference between BPETs and LPET, we could describe the crystallization characteristics of BPET with reason. The presence of branching brought two opposite effects on crystallization. Branching architecture reduced nucleating rate and nucleation density, which would diminish the rate of crystallization, because more time was required to exclude the branching points from crystal nucleates. The study on crystallization behavior of poly(ethylene terephthalate) and its copolymers containing isophthalate units (IPT) showed that slower crystallization enabled more effective exclusion of IPT units from the crystal region [18]. On the other hand, branching provides more free volume (lower T_g as found in Fig. 2), which was in favor of growth of crystallization due to more motion of polymer chains. Moreover, low nucleation density made less truncation of spherulites, which allowed spherulites to grow in more perfect three-dimension possible in BPET, whereas crystallization growth developed mainly in planar two-dimension, and the second nucleating could happen on the surface of growing crystals for LPET.

Comparing the values of $t_{1/2}$ and t_{max} , it was found that the t_{max} value of each sample was smaller than that of its corresponding $t_{1/2}$ values. However, the t_{max} of each BPET was closer to its corresponding $t_{1/2}$ than that of LPET. It could be hinted that BPETs reached their maximum crystallization rate later than LPET, at about 50% crystallization conversion. Therefore, although the onset of crystallization of LPET came earlier than that of BPETs, the growing rate of crystallization of LPET during the whole crystallization period still hung behind BPETs.

To sum up, the presence of branching was a kind of defect for macromolecular chains to crystallize. More time was needed for BPETs to nucleate, so longer induced time for BPETs was found. During the studied extent of branching, the overall rate of crystallization of BPETs was faster than that of LPET, mainly resulted from the rapid growth rate of crystallization of BPETs. Smaller number of nucleates for BPET would be formed owing to reduced nucleation sites, hence more perfect geometric growth of crystallization in three-dimension could developed in BPET due to less truncation of spherulites, otherwise the growth of crystallization in LPET showed mostly two-dimensional or in plate-like or disc-like way.

While branching was in high degree, the blocking of branching to the crystallization could play a prior role. This might be why our result was different from Jakannan and co-workers [16]. High concentration of branching (1.4–5 mol%) was employed in their work. They found that n values of BPET varied from 1 to 2, suggesting a rod like growth process compared to a spherulitic one observed in PET. At the same time, they also found the presence of branching in small concentration appeared to enhance the crystallization. At high concentration of such defects, however the crystallization process was slowed down. But

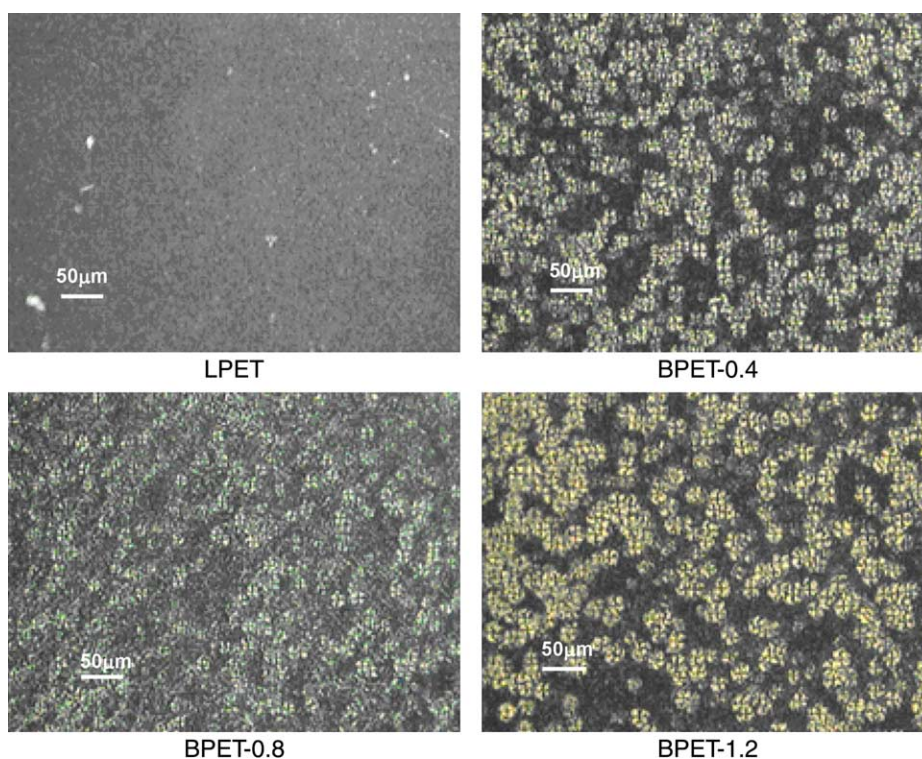


Fig. 8. The crystallization morphologies observed from POM for both LPET and BPETs ($t = 300$ s).

Jayakannan interpreted the rapid crystallization of small branched PETs as facilitated nucleation [16].

3.4. Observation of crystallization morphologies by POM

All samples were put between two circle shaped glass slides, melted fully firstly, then cooled to 220 °C at the maximum rate. Time counting began when the temperature reached 220 °C. The time from the beginning to the appearance of the first brightness in visual field was taken as the induced time for crystallization. Table 4 lists the induced time of crystallization for all samples at 220 °C.

The direct observation of induced time of crystallization was in agreeable with the result of isothermal crystallization kinetics via DSC. As mentioned above, compared with LPET, BPETs needed more time to exclude branching points and form nucleates. On the other hand, once nucleates were formed, BPETs made the evolution of crystallization more rapidly than LPET. The crystal morphologies for all samples obtained by shooting at the same crystallization time were shown in Fig. 8. It was obvious that the cross patterns which stands for the spherular crystal in BPETs were more perfect and greater than that in LPET. This meant that the development of crystallization was in more perfect three-dimension in BPET than in LPET. The crystallization morphological behavior of reactively processed PBT/epoxy blends also showed the similar result. It was found that the radius of spherulities increased gradually up to 30% epoxy resin, because there was enough space for spherulities to grow duo to dilution effect [19].

The different crystallization morphologies between BPET and LPET could be as evidence that branching hampers nucleation. So more induced time, smaller number of nucleates, increased radius of spherulities, enhanced rate of crystallization could be considered as characteristics of crystallization of BPETs.

4. Conclusions

Branched poly(ethylene terephthalate) samples (BPETs) were obtained from polycondensation by incorporation of trifunctional glycerol from 0.4–1.2 mol%. BPETs showed different crystalline behavior when compared with linear PET. The crystalline temperatures T_{cc} from the melt shifted to high temperatures and the T_{hc} from the glass state decreased for BPETs. Very small amount (0.4–0.8 mol%) introduction of GL enhanced the crystallinity, but high amount (1.2 mol%) made the crystallinity reduced. In addition, branching brought little influence on the melting points of polymers within the branching range investigated. The kinetics of isothermal crystallization announced that the studied extent of branching made the overall rate of crystallization increased, especially at low crystallization temperature and at low branching extent. At the same time, branching prolonged the induced time. More time was required to exclude the branching from crystallization. Therefore the quick growing rate of crystallization made great contribution to the overall rate of crystallization for BPETs. The presence of branching reduced the nucleation sites, which made BPETs develop crystallization in more perfect three-dimension due to

less truncation of spherulites. More integral and perfect patterns of spherulites of BPETs were observed from POM, which matched the greater values of n for BPETs.

References

- [1] Yuan CM, Di Silvestro G, Speroni F, Guaita C, Zhang HC. Control of macromolecular architecture of polyamides by poly-functional agents. *Macromol Symp* 2003;199:109–24.
- [2] Khotina IA, Shmakova OE, Baranova DY, Burenkova NS, Gurskaja AA, Valetsky PM. High branched polyphenylenes with 1,3,5-triphenylbenzene fragments via cyclocondensation of a cerylaromatic compound and nickel-catalyzed dehalogenation: synthesis and light emission. *Macromolecules* 2003;36(22):8353–60.
- [3] Schwartz SA, Lee SJ, Chan A. The use of comb-branched copolymers as pigment dispersants. International conference on digital printing technologies, New Orleans, LA, United States 2003.
- [4] Mecerreyes D, Huang E, Magbitang T, Volksen W, Hawker CJ, Lee VY. Application of hyper branched block copolymers as templates for the generation of nano porous organosilicates. *High Perform Polym* 2001; 13(2):S11–S19.
- [5] Kharchenko SB, Kannan RM, Cernohous JJ, Venkataramani S, Babu GN. Unusual contributions of molecular architecture to rheology and flow birefringence in hyper branched polystyrene melts. *J Polym Sci, Part B: Polym Phys* 2001;39(21):2562–71.
- [6] Yilmazer U, Xanthos M, Bayram G, Tan V. Viscoelastic characteristics of chain extended/branched and linear polyethylene terephthalate resins. *J Appl Polym Sci* 2000;75(11):1371–7.
- [7] Hess C, Hirt P, Oppermann W. Influence of branching on the properties of poly(ethylene terephthalate) fibers. *J Appl Polym Sci* 1999;74:728–38.
- [8] Jayakannan M, Ramakrishnan S. Synthesis and thermal analysis of branched and kinked polyethylene terephthalate. *J Polym Sci, Part A: Polym Chem* 1998;36(2):309–17.
- [9] Rosu RF, Shanks RA, Bhattacharya SN. Synthesis and characterization of branched poly(ethylene terephthalate). *Polym Int* 1997;42(3):267–75.
- [10] Oh SJ, Kim BC. Effects of hydroxyl-group end capping and branching on the physical properties of tailored polyethylene terephthalates. *J Polym Sci, Part B: Polym Phys* 2001;39:1027–35.
- [11] Japon S, Bough L, Leterrier Y, Manson J-AE. Reactive processing of poly(ethylene terephthalate) modified with multifunctional epoxy-based additives. *Polymer* 2000;41(15):5809–18.
- [12] Champagne MF, Gendron R, Huneault MA. Branched polyethylene terephthalate foaming using HFC-134a: on-line process monitoring. Annual technical conference—ANTEC, conference proceedings. vol. 2 2003 p. 1870–74.
- [13] Hudson N, MacDonald WA, Neilson A, Richards RW, Sherrington DC. Synthesis and characterization of nonlinear PETs produced via a balance of branching and end capping. *Macromolecules* 2000;33:9255–61.
- [14] Japon S, Luciani A, Nguyen QT, Leterrier Y, Manson J-AE. Molecular characterization and rheological properties of modified poly(ethylene terephthalate) obtained by reactive extrusion. *Polym Eng Sci* 2001;41(8): 1299–309.
- [15] Rosu RF, Shanks RA, Bhattacharya SN. Dynamic rheology of branched poly(ethylene terephthalate). *Polym Int* 2000;49:203–8.
- [16] Jayakannan M, Ramakrishnan S. Effect of branching on the crystallization kinetics of poly(ethylene terephthalate). *J Appl Polym Sci* 1999;74:59–66.
- [17] Liu W, Debelak KA, Witt AR, Yang CK, Collins WE, Lott C. Structural features of crystallized poly(ethylene terephthalate) polymers. *J Polym Sci, Part B: Polym Phys* 2002;40:245–54.
- [18] Lee B, Shin TJ, Lee SW, Ree M. Time-resolved X-ray scattering and calorimetric studies on the crystallization behaviors of poly(ethylene terephthalate) (PET) and its copolymers containing isophthalate unites. *Polymer* 2003;44:2509–18.
- [19] Kulshreshtha B, Ghosh AK, Misra A. Crystallization kinetics and morphological behavior of reactively processed PBT/epoxy blends. *Polymer* 2003;44:4723–34.